SYNTHESIS AND CHARACTERIZATION OF DOPED ZINC SILICATE PHOSPHORS FOR OPTOELECTRONIC APPLICATIONS

A SYNOPSIS

Submitted by

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(Reg. No. 201915142)

in partial fulfilment for the award of the degree of

DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

SCHOOL OF ADVANCED SCIENCES

KALASALINGAM ACADEMY OF RESEARCH AND EDUCATION

(DEEMED TO BE UNIVERSITY)

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TAMIL NADU, INDIA

JUNE 2023

1. INTRODUCTION

In recent decades, the market for optoelectronic technology was quite expensive in the beginning, but with advancements, its price is decreasing day by day with more and more increasing efficiency. The extensive usage of inorganic phosphor materials, such as lighting, displays, sensors, etc., causes them to advance very quickly. Due to their more significant energy requirements for lighting and shorter lifespan, traditional light sources, including incandescent bulbs, halogen lamps, fluorescent lamps, and others, have disadvantages. Light-emitting diodes (LEDs) are the most often used in various applications due to their enhanced attributes, such as low energy consumption for illumination and a long lifespan [1]. Since lighting accounts for 20% of all electricity consumption globally, LEDs have embraced the challenge of lowering lighting power consumption [2]. LEDs, incandescent and fluorescent bulbs are currently miles ahead of their competitors [3]. The materials with photoluminescent qualities are the ones that are being pursued and studied the most among the various classes of materials utilized to make LEDs today that enhance people's lives [4]. Besides lighting applications, new avenues are available to focus technological development towards optoelectronic applications. Now, there is a focus on developing photoluminescent materials with more productivity on their characteristics and improved reliability in their constituent features [5]. Because of its anticipated uses in optics [6], sensors [7], optoelectronics, photonics [8], solar cells [9], scintillators [10], light-emitting diodes (LEDs) [11], lasers [12], etc., the luminous capabilities of inorganic materials, in particular, are very enticing [13].

Good chemical/thermal stability, and low production cost, should be required to achieve the technological development in the optoelectronic applications. It leads to search the alternative phosphors to overcome their limitations for emerging applications. Silicates are the alternatives due to their high chemical/ thermal stability compared to above mentioned phosphors, high luminescence efficiency, easy preparation recipe, good moisture resistance and low production cost[11]. In particular, willemite, also known as zinc silicate (Zn_2SiO_4), is one of the most often used inorganic luminous materials [14] due to their properties. It is also widely known that zinc silicate is polymorphic and may exist in several phases [15]. Studies on zinc silicates have been recognized for their

revolutionary significance. These materials exhibit exceptional dielectric characteristics, strong mechanical qualities, excellent electrical conductivity, and thermal conductivity. J.B. Yoo et al. reported on the controlled thermal hydrolysis production of luminous Mn-doped Zn_2SiO_4 microspheres [16]. Novel phosphors have become more sought-after in recent years due to their effectiveness in field emission displays for future generations [17–21]. There have been numerous new doping methods proposed, including electrospinning method [22], combustion method [23], polymer precursor method [24], spray pyrolysis method [25], sol-gel method [26], hydrothermal method [27], sputtering method [28], sonochemistry method [24], solvothermal method [29], co-precipitation method [30], and solid state reactions method [31]. Sol-gel and hydrothermal techniques are the easiest and most economical techniques. Among the other techniques, the hydrothermal and sol-gel procedures are used to synthesize Zn_2SiO_4 phosphors, which have several uses in a variety of industries. structural and optical properties of Zn_2SiO_4 phosphors can be controlled by doping the elements such as Li, Bi, Ni, V, Mn, Eu and Tb, Mn, Ce, Tb, Eu, etc. as dopants [32 - 33].

2. REVIEW OF LITERATURE

Literature survey is the comprehensive and extensive examination of several research works done by researchers on a selected field and the briefing of their findings. At the present day the attention of workers in science, technology and engineering has been drawn to the preparation and characterization to analyze their properties of Zn_2SiO_4 phosphor for the desired applications. The details of reported Zn_2SiO_4 phosphor materials for the different applications are given in the Table 2.1.

Table 2.1. Reported of Zn_2SiO_4 phosphor materials based on different dopant with Photoluminescence behaviour

S. No.	Material	Preparation Method	Excitation wavelength (nm)	Emission wavelength (nm)	Year
1.	$Zn_2SiO_4:Mn^{2+}$	Solid state	254	529	2010 Y.Il Kim *et al.* [34]

S. No.	Material	Preparation Method	Excitation wavelength (nm)	Emission wavelength (nm)	Year
2.	Mn^{2+}:Zn_2SiO_4-Eu^{3+}:Gd_2O_3	hydrothermal	255	580,612, 625	2017 F.Huang *et al.* [35]
3.	Zn_2SiO_4:V	Sol-gel	350	540,760	2012 J. El Ghoul *et al.* [36]
4.	Cu^{2+}:Zn_2SiO_4, Ni^{2+}:Zn_2SiO_4 and Co^{2+}:Zn_2SiO_4	Sol-gel	Cu^{2+}:Zn_2SiO_4 – 355,414 Ni^{2+}:Zn_2SiO_4 – 317,407 Co^{2+}:Zn_2SiO_4 – 384,442	Cu^{2+}:Zn_2SiO_4 – 455 Ni^{2+}:Zn_2SiO_4 – 506 Co^{2+}:Zn_2SiO_4 – 484	2014 B. Chandra Babu *et al.* [37]
5.	Zn_2SiO_4:Eu^{3+}	sol–emulsion–gel method	249	613	2004 A.Patra *et al.* [38]
6.	Zn_2SiO_4:Mn	Gel combustion	251	522	2007 P.Thiyagarajan *et al.* [39]
7.	α- and β-Zn_2SiO_4: Mn	Solvothermal	245	525, 563	2010 Y. Jiang *et al.* [29]

S. No.	Material	Preparation Method	Excitation wavelength (nm)	Emission wavelength (nm)	Year
8.	$Zn_2SiO_4:Mn^{2+}$	Glycothermal reactions	250	522	2011 K. Uegaito *et al.* [40]
9.	$Zn_2SiO_4:Yb^{3+}$, Er^{3+} by co-doping with Li+ or Bi^{3+}	Microwave processing	254	525,547,660	2012 L. Jiang *et al.* [32]
10.	Ce $^{3+}$/Mn^{2+} β-Zn_2SiO_4	conventional melt-quenching method	345	430, 575	2013 R. Ye *et al.* [41]
11.	$Zn_2SiO_4:Re^{3+}$ (Eu, Dy, Sm)	Solution combustion technique	Eu^{3+} 393 Dy^{3+} 349 Sm^{3+} 401	Eu^{3+} = 534, 590, 613,648,700 Dy^{3+} = 482, 573, 665 Sm^{3+}=554,599,668,720	2015 R. B. Basavaraj *et al.* [42]
12.	Zn_2SiO_4: Eu^{2+}	Melt quenching technique	400	600	2016 N. A. S. Omar *et al.* [43]
13.	Zn_2SiO_4	Precipitation	355	411, 455, 480, 528	2018 E. A. G. E. Ali *et al.* [44]

S. No.	Material	Preparation Method	Excitation wavelength (nm)	Emission wavelength (nm)	Year
14.	Zn_2SiO_4	Thermal Treatment Method	350	423, 447, 484, 530	2018 I. M. Alibe *et al.* [45]
15.	α-Zn_2SiO_4: Mn^{2+}	Ball milling	260	525	2019 L. T. T. Vien *et al.* [46]
16.	Zn_2SiO_4:Er^{3+}	conventional melt quenching method	385	599	2019 N. Effendy *et al.* [47]
17.	Sm^{3+} and Mn^{2+} incorporation Zn_2SiO_4	Gel combustion	396	564,600,648 ,706	2021 Z. G. Portakal-Ucar *et al.* [48]

From our literature survey, there are a very few reports on (V^{5+}, Nb^{5+}, and La^{3+}) doped Zn_2SiO_4 phosphors prepared through sol-gel technique for the getting different colour emission. Also, PLQY of the phosphors for Mn^{2+} and Eu^{3+} doped Zn_2SiO_4 phosphors have to be concentrated for further developments.

This present thesis focuses on the synthesis and characterization of Transition Metal (TM) (Mn^{2+}, V^{5+}, and Nb^{5+}) and Rare Earth(RE) (Eu^{3+} and La^{3+}) doped Zn_2SiO_4 phosphors. The systematic study has done for the above proposed phosphors from structural to photoluminescence analysis for getting different colour emissions for optoelectronic applications.

3. RESEARCH PROBLEMS

The global phosphor market is estimated to be worth $450 million annually, with growth rates expected to range between 8 and 10%. Additionally, they must compete with and outperform a variety of display technologies and applications, such as liquid crystal, plasma, LEDs, OLEDs, automobiles, and field emission, all of which need an expanding variety of phosphor types to meet both new and ongoing demands. They include applications for image panels, cathodic, electroluminescent, plasma, LED, colour conversion, micro display, and xenon activation. To produce more effective and stable phosphors with better ageing and half-life features, novel chemicals, material properties, formats, and processes including doping activation, particle sizes, coatings, and even nanocrystals being studied in an environment of increased awareness. All of these will have an impact on the market's supply, demand, cost, and business development possibilities as it continues to expand in both volume and value.

Transition Metal / Rare Earth doped Nitrates, Sulphides, Borates, Gallates, Molybdates, Oxides, and Tungstates, phosphors produce excellent luminescence performance. However, good chemical/thermal stability, and low production cost, should be required for the achieving the technological development in the optoelectronic applications and this motivates the investigators to search the alternative phosphors to overcome their limitations for emerging applications. Silicates are the alternatives due to their high chemical/ thermal stability compared to above mentioned phosphors, high luminescence efficiency, easy preparation recipe, good moisture resistance and low production cost. In particular, zinc silicates are good alternatives due to high electronegativity, high centroid shift, excellent chemical and thermal stability, colour-tuning properties and cost-effectiveness. Different colour emissions from the Zinc Silicate host by adding the dopants must be systematically studied to get new ventures for optoelectronic applications.

4. OBJECTIVES

The objective of the present thesis is to synthesis the undoped, transition and rare earth metals like Mn^{2+}, V^{5+}, Nb^{5+}, Eu^{3+}, and La^{3+}doped Zn_2SiO_4 phosphors using Sol-gel and hydrothermal methods. For the purpose of this research, the following six series of phosphor materials have been selected:

i. Zn_2SiO_4 (at 700 °C, 800 °C, 900 °C, 1000 °C and 1100 °C)
ii. $Zn_{2-x}Mn_xSiO_4$ (x = 0%, 1%, 2%, 3%, 4% and 5%)
iii. $Zn_{2-x}V_xSiO_4$ (x = 0%, 2%, 4%, 6%, 8%, and 10%)
iv. $Zn_{2-x}Nb_xSiO_4$ (x = 0%, 2%, 4%, and 6%)
v. $Zn_{2-x}Eu_xSiO_4$(x = 0%, 2%, 3%, 4.5% and 6%)
vi. $Zn_{2-x}La_xSiO_4$(x = 0%, 2%, 4%, and 6%)

The following is a brief summary of the present research works:

- To synthesize the Zn_2SiO_4 phosphor by hydrothermal and sol-gel technique.
- To investigate the synthesized phosphor materials using powder X-ray diffraction (PXRD) for structural investigation.
- To analyze the surface morphological and microstructure properties of the phosphor by scanning electron microscopy (SEM) and Field Emission Scanning Electron Microscopy (FE-SEM).
- To analyze the elemental compositions of the materials qualitatively and quantitatively using Energy dispersive X-ray diffraction (EDAX).
- To determine the optical energy band gap (E_g) for all the materials by UV-visible Diffuse reflectance spectra employing Kubelka-Munk method through UV-vis DRS.
- To investigate the Photoluminescence (PL), Photoluminescence Quantum Yield (PLQY) and PL decay time measurements of prepared phosphors materials.

5. SCOPE OF THE PRESENT WORK

The plenty of luminescent phosphors are used for various display applications in India, which are imported from foreign nations like China, Japan, Korea, the United Kingdom, and the United States due to the cost effect of rare earth elements and the industrial-scale knowledge in producing highly sensitive phosphors. In our work, silicate-based materials are preferred due to their adaptability, low-cost transition metals (particularly Mn^{2+}, V^{5+}, and Nb^{5+}) and rare earth (mainly La^{3+} and Eu^{3+}) doped zinc silicates, high luminescence efficiency, widespread applications, sample preparation methods, and moisture stability. Fluorescent lights, neon discharge lamps, oscilloscopes, colour televisions, and many other displays and lighting equipment utilize activated silicate

phosphors that are exposed to rare earth ions and transition metal ions as light emitting materials. Because of its chemical stability, high luminescence efficiency, and semiconducting properties, transition metals (Mn^{2+}, V^{5+}, and Nb^{5+}) doped zinc silicate is commonly used as a green-emitting, Blue-green emitting, and blue emitting phosphor material, and rare earth (La^{3+} and Eu^{3+}) doped zinc silicate is widely used as a red emitting for PDPs and CRTs. It is crucial to manufacture phosphors with high luminous efficiency, tiny particle sizes, controlled topology, high crystallinity, and well-doped impurities for these applications. The production technique heavily influences the luminescence characteristics of phosphor particles. Thus, it's essential to develop a process that can control the surface morphology, size, composition, and purity of the prepared nanophosphor particles. The technique must be low cost, easy to process, high production rate, and capable of creating high purity materials at high yields in order to be adopted to make phosphor particles. Also, La^{3+} doped Zn_2SiO_4 phosphor introduces the new ventures in the optoelectronic applications due to their NIR emissions. In the present study, Zn_2SiO_4:Mn^{2+} (Green), Zn_2SiO_4:V^{5+} (Blue-Green), Zn_2SiO_4:Nb^{5+} (Blue), Zn_2SiO_4:Eu^{3+} (Red), and Zn_2SiO_4:La^{3+} (Near Infra-red), phosphors have been successfully synthesized by conventional sol-gel synthesis and hydrothermal method.

6. ORGANIZATION OF THESIS

The present doctoral research work consists of ten chapters and the contents of the chapters are given below.

CHAPTER I – INTRODUCTION

This chapter gives the general introduction about the properties of luminescence, types of luminescence, Fluorescence and Phosphorescence, Mechanism of Photoluminescence, and photoluminescence applications.

CHAPTER II – LITERATURE SURVEY

The brief literature survey Zn_2SiO_4 phosphor materials based on different dopant with Photoluminescence behaviour was studied. From the complete literature survey, the pure α-Zn_2SiO_4 phosphors and different (Mn^{2+}, V^{5+}, Nb^{5+}, Eu^{3+}, and La^{3+}) doped Zn_2SiO_4 phosphors were carried out to provide important information towards LEDs application materials and methods. The research problem and objective of the proposed work is also provided in this chapter.

CHAPTER III – PREPARATION AND CHARACTERIZATION TECHNIQUES

The different synthesis methods and the characterization techniques of Zn_2SiO_4 phosphor materials are detailed out in this chapter. Among the various synthesis methods, sol-gel and hydrothermal technique has been briefly explained in this chapter. Also, briefly discussed about the characterization techniques such as Powder X-Ray diffractometer (PXRD), Scanning Electron Microscopy (SEM) and Field Emission Scanning Electron Microscopy (FE-SEM), Energy dispersive X-ray diffraction (EDAX), Diffuse Reflectance Spectroscopy (DRS), Photoluminescence (PL), Photoluminescence Quantum Yield (PLQY) and Photoluminescence decay life time (TRPL).

CHAPTER IV – EFFECT OF CALCINATION TEMPERATURE ON α-Zn_2SiO_4 PHOSPHORS

The Zn_2SiO_4 phosphor was synthesized by a hydrothermal approach with different calcination temperatures. The present investigation deals with the effect of calcination temperature on the various analytical and spectroscopical techniques were used to examine the structural, morphology and optical properties of Zn_2SiO_4 phosphor. Structural studies done by X-ray diffraction studies revealed the rhombohedral crystal structure with (140) plane as a preferred orientation in Zn_2SiO_4. Hexagonal shape morphology was observed in the Zn_2SiO_4 materials. At 900 ºC, Zn_2SiO_4 material achieved the optimized structures with high crystallinity. Optical band gap values are found to be in the range of 5.39 – 5.00 eV while changing the calcination temperature of Zn_2SiO_4 phosphors.

CHAPTER V – INVESTIGATIONS OF Mn-DOPED Zn_2SiO_4 PHOSPHORS FOR GREEN EMISSION

High-purity α-Zn_2SiO_4: x% Mn (x = 0, 1, 2, 3, 4, and 5) phosphors were synthesized by the conventional hydrothermal approach. The effects of Mn^{2+} doping on the structural and optical properties of Zn_2SiO_4 were investigated. In PL studies, Zn_2SiO_4:4% Mn phosphor gave intense 525 nm green emission due to radiative transitions from the $^4T_1$ (4G) excited state to the $^6A_1$ (6S) ground state of Mn^{2+} ions. Lifetime measurements for all the prepared samples were carried out, and the optimal Zn_2SiO_4:4% Mn phosphor was around 52 ns. The bandgap energy and morphology were also studied by UV–Vis DRS and SEM characterization techniques, respectively. The structural and luminescence properties of

Mn-doped Zn_2SiO_4 phosphor have been investigated in detail, suggesting that hydrothermally assisted Mn-doped Zn_2SiO_4 can be used as a lighting applications.

CHAPTER VI – INVESTIGATIONS OF V-DOPED Zn_2SiO_4 PHOSPHORS FOR GREEN EMISSION

Vanadium (V) doped zinc silicate phosphor was prepared by the sol-gel method. The phase-pure rhombohedral structure was identified in PXRD analysis. The 8 wt. % Zn_2SiO_4: V showed the least volume of the unit cell and microstrain than the other V-doped samples. The SEM analysis confirmed the uniformity of the grain distribution for 8 wt. % of the V-doped Zn_2SiO_4 sample. The elements of the samples and the purity of the samples were confirmed by EDX analysis. When vanadium is added to Zn_2SiO_4 phosphors, the energy band gap (E_g) changes from 5.29 to 2.66 eV. The PL study confirmed the blue and green emissions. The emission transition and average decay lifetimes were observed. The prepared material exhibited a maximum quantum yield of 7.06% for the 8 wt. % V-doped Zn_2SiO_4 sample. This concluded that an 8 wt. % V-doped Zn_2SiO_4 sample could be a promising material for display and lighting applications.

CHAPTER VII – INVESTIGATIONS OF Nb-DOPED Zn_2SiO_4 PHOSPHORS FOR BLUE EMISSION

Niobium (Nb) doped zinc silicate (Zn_2SiO_4) by varying different wt. % of Nb was synthesized through the sol-gel method at 1200 °C under normal atmospheric conditions. The phase pure rhombohedral structure was identified in PXRD analysis. The Rietveld refinement study examined the structural analysis and it confirms the structural distortion due to the Nb dopant effect in the Zn_2SiO_4 host and 4 wt. % Nb-doped Zn_2SiO_4 showed the least volume of the unit cell and microstrain than the other Nb-doped samples. Photoluminescence analysis confirmed that luminescence behaviour lies in the blue region. The synthesized material displays a maximum quantum yield of 15.54% for the 4 wt. % Nb doping Zn_2SiO_4. The CIE graph also proved the blue emission of the prepared samples. The lowest band gap of 4wt. % Nb-doped Zn_2SiO_4 reveals the enhanced PL emission intensity. 4wt % of Nb-doped Zn_2SnO_4 demonstrates the highest average lifetime at 21.6 ns. This concluded that 4 wt. % Nb-doped Zn_2SiO_4 particles can be a prominent material for LED applications.

CHAPTER VIII – INVESTIGATIONS OF Eu-DOPED Zn_2SiO_4 PHOSPHORS FOR RED EMISSION

Europium (Eu) doped Zn_2SiO_4 ($Zn_{2-x}Eu_xSiO_4$, x = 0, 0.02, 0.03, 0.04.5, and 0.06) phosphor with varying weight percentages were synthesized using the hydrothermal process. The phase-pure rhombohedral structure was discovered by PXRD analysis. In the FESEM pictures supported the presence of sphere shape-like particles. The element purity of the sample was analyzed using EDX. The optical energy band gap is decreased from 5.01 to 3.20 eV upto 4.5 wt.% of Eu^{3+} using UV-vis DRS. The red emission peak shown on the CIE graph and the red emission peak at 615 nm were both confirmed by PL analysis. The TRPL transition and average decay lifespan values of 32.8 ns were found at 4.5 wt. % of Eu^{3+}. Findings suggested that Zn_2SiO_4 phosphors with a 4.5 wt. % Eu^{3+} doping could be a promising material for applications requiring display devices.

CHAPTER IX – INVESTIGATIONS OF La-DOPED Zn_2SiO_4 PHOSPHORS FOR NIR EMISSION

Lanthanum (La) doped with zinc silicate (Zn_{2-x} La_xSiO_4 (x = 0.00, 0.02, 0.04 and 0.06) phosphors were synthesized using the sol-gel process. PXRD investigation revealed the phase-pure rhombohedral structure. FESEM pictures supported the presence of sphere-like particles. Using EDX, the materials element purity was examined. When La^{3+} ions doping increased from 0 wt. % to 6 wt. %, the optical band gap of La-doped Zn_2SiO_4 materials decreased from 5.10 eV to 3.80 eV. The prepared material displays a maximum PL quantum yield of 12.92% for 4 wt. % La doped Zn_2SiO_4 sample. PL analysis confirmed the red emission peak at 730 nm and also bluish green demonstrated using the CIE graph. At 4 wt. % La, the TRPL transition, and average decay lifetime values of 30.4 ns were detected.

CHAPTER X – CONCLUSION

This chapter provides significant findings drawn from the present doctoral research work. Also, it provides the suggestions for the future studies towards the optoelectronic applications.

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